

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 917 228 A1**

(12)

**EUROPEAN PATENT APPLICATION**

published in accordance with Art. 158(3) EPC

(43) Date of publication:  
19.05.1999 Bulletin 1999/20

(51) Int. Cl.<sup>6</sup>: **H01M 10/40**, H01M 4/58,  
H01M 4/02

(21) Application number: **98921899.5**

(86) International application number:  
**PCT/JP98/02400**

(22) Date of filing: **29.05.1998**

(87) International publication number:  
**WO 98/54779 (03.12.1998 Gazette 1998/48)**

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **30.05.1997 JP 141920/97**

(71) Applicants:

- **MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.**  
Kadoma-shi, Osaka 571-0050 (JP)
- **MITSUBISHI CHEMICAL CORPORATION**  
Chiyoda-ku, Tokyo 100-0005 (JP)

- **SUGIMOTO, Toyoji,**  
Matsushita Elect. Ind. Co., Ltd  
Osaka 571-0050 (JP)
- **YAMAGUCHI, Shoji,**  
Mitsubishi Chemical Corporation  
Inashiki-gun, Ibaraki 300-0332 (JP)
- **HAYASHI, Manabu,**  
Mitsubishi Chemical Corporation  
Inashiki-gun, Ibaraki 300-0332 (JP)

(72) Inventors:

- **KITAGAWA, Masaki,**  
Matsushita Elect. Ind. Co., Ltd  
Osaka 571-0050 (JP)
- **KOSHINA, Hizuru,**  
Matsushita Elect. Ind. Co., Ltd  
Osaka 571-0050 (JP)

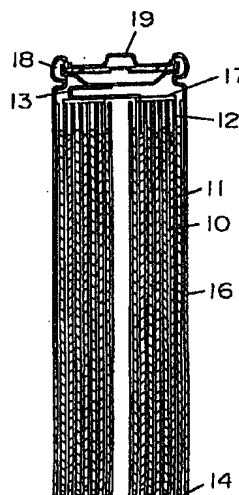
(74) Representative:

**Rackham, Stephen Neil**  
**GILL JENNINGS & EVERY,**  
Broadgate House,  
7 Eldon Street  
London EC2M 7LH (GB)

(54) **NONAQUEOUS ELECTROLYTE SECONDARY BATTERY**

(57) Enhancement of the storage property at a high temperature and discharge characteristics at a low temperature of a nonaqueous electrolyte secondary cell is intended. A negative electrode material which is prepared by covering the surface of a nucleus made of a graphite powder with a carbonaceous matter, the graphite powder having a specified plane interval, spectrum value, mean particle size, specific surface area, tapping density, and (110)/(004) X-ray peak intensity ratio, is used in the nonaqueous electrolyte secondary cell.

**FIG. 2**



**EP 0 917 228 A1**

## Description

## TECHNICAL FIELD

- 5 [0001] The present invention relates to a nonaqueous electrolyte secondary cell, and more particularly to a carbon material for negative electrode of a lithium ion secondary cell.

## BACKGROUND ART

- 10 [0002] As a nonaqueous electrolyte secondary cell, a so-called lithium secondary cell has been hitherto studied in the interest of higher energy density by means of higher voltage and larger capacity, in which metal lithium is used as a negative electrode active material, whereas oxide, sulfide, selenide or other chalcogen compounds of transition metal, such as manganese dioxide, molybdenum disulfide or titanium selenide is used as a positive electrode active material, and organic electrolyte made of organic solvent solution of lithium salt is used as a nonaqueous electrolyte. In this lithium secondary cell, however, while an interlayer compound which exhibits relatively good charge and discharge characteristics may be selected as a positive electrode active material, the charge and discharge characteristics of metal lithium for negative electrode are not particularly excellent. Thus, the cycle life for repeating charge and discharge can hardly be extended, and moreover, there is a danger that heat generation may be caused by internal short-circuit, presenting a problem in safety. More specifically, the metal lithium in the negative electrode active material elutes into the organic electrolyte as lithium ions by discharge. When the eluted lithium ions precipitate on the surface of the negative electrode as metal lithium by charge, not all of them precipitate smoothly as in the initial state, but some precipitate as active metal crystals in the form of dendrite or moss. The active metal crystals decompose the organic solvent in the electrolyte, while the surface of the metal crystals is covered with a passive film to be inactivated, hardly contributing to discharge. As a result, as charge and discharge cycles are repeated, the negative electrode capacity declines, wherefore the negative electrode capacity had to be set extremely larger than that of the positive electrode when fabricating a cell. Besides, the active dendritic metal lithium crystals may pierce through the separator and contact with the positive electrode, possibly causing internal short-circuit. By internal short-circuit, the cell may generate heat.

- 25 [0003] Accordingly, the so-called lithium secondary cell, which uses a carbon material that is capable of repeating reversibly intercalation and deintercalation by charge and discharge as the negative electrode material, has been proposed, is now being intensively researched and developed, and is already put in actual use. In this lithium secondary cell, so far as it is not overcharged, active dendritic metal lithium crystals do not precipitate on the negative electrode surface when the cell is charging up and discharging, and enhancement of safety is much expected. Moreover, since this battery is extremely superior in high rate charge and discharge characteristics and cycle life to the lithium secondary cell using metal lithium in the negative electrode active material, the demand for this battery is growing rapidly in recent years.

- 35 [0004] As the positive electrode active material for lithium ion secondary cell of 4V class, a composite oxide of lithium and transition metal, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ , and  $\text{LiMn}_2\text{O}_4$ , corresponding to the discharge state is being employed or considered. As the electrolyte, similarly as in the lithium secondary cell, a nonaqueous electrolyte such as organic electrolyte and polymer solid electrolyte is used.

- 40 [0005] When graphite is used in the negative electrode material, the theoretical value of capacity per 1 g of carbon by reference to  $\text{C}_6\text{Li}$  of interlayer compound produced by intercalation of lithium ion is 372 mAh. Therefore, among various carbon materials, the one which helps realize a specific capacity close to this theoretical value, as well as causes the capacity per unit volume, i.e., capacity density (mAh/cc) to be as high as possible, should be selected for the negative electrode that is put in practical use.

- 45 [0006] Among various carbon materials, in the hardly graphitized carbon generally known as hard carbon, materials which exhibit a specific capacity exceeding the above mentioned theoretical value (372 mAh/g) are discovered and are being investigated. However, since the hardly graphitized amorphous carbon is small in true specific gravity and is bulky, it is substantially difficult to increase the capacity density per unit volume of the negative electrode. Furthermore, there still remain many problems, for example, the negative electrode potential after charge is not so base as to be close to the metal lithium potential, and flatness of discharge potential is inferior.

- 50 [0007] By contrast, when natural graphite or artificial graphite powder which is high in crystallinity is used in the negative electrode, the potential after charge is close to the metal lithium potential, and the flatness of discharge potential is excellent, whereby the charge and discharge characteristics are enhanced as a practical battery, and thus the graphite powder is recently becoming the mainstream of negative electrode material.

- 55 [0008] However, when the mean particle size of the graphite powder for negative electrode of a lithium ion secondary cell is large, the charge and discharge characteristics at high rate and discharge characteristic at low temperature tend to be inferior. Accordingly, by reducing the mean particle size of the powder, the high rate charge and discharge characteristics and low temperature discharge characteristic are enhanced, but if the mean particle size is made too small,

the specific surface area of the powder becomes too large, as a result of which there is a problem of increased irreversible capacity, in which the lithium inserted by first charge in the powder cannot contribute to discharge after the first cycle. This phenomenon is not only a fatal demerit for enhancement of energy density, but also causes the solvent in the organic electrolyte to be decomposed in case the battery is left at a high temperature exceeding 100°C, which may lead to self-discharge as well as an electrolyte leak accident due to raise in the cell internal pressure, thereby lowering the reliability of the battery.

[0009] It is hence easily understood that the appropriate specific surface area and mean particle size are essential for the graphite powder for negative electrode. An invention proposed from such viewpoint is, for example, Japanese Laid-open Patent No. 6-295725, which uses graphite powder of which specific surface area by BET method is 1 to 10 m<sup>2</sup>/g, mean particle size is 10 to 30 microns, and at least one of the content of powder with a particle size of 10 microns or less and the content of powder with a particle size of 30 microns or more is 10% or less. Further, in Japanese Laid-open Patent No. 7-134988, the usage of spherical graphite powder is disclosed, which is obtained by graphitizing meso-carbon micro-beads formed by heating petroleum pitch at a low temperature and of which plane interval (d002) of (002) plane by wide angle X-ray diffraction method is 3.36 to 3.40 angstroms, and specific surface area by BET method is 0.7 to 5.0 m<sup>2</sup>/g. Further, Japanese Laid-open Patent No. 5-307959 discloses the use of a multi-phase carbon matter having a specific surface area that is 20 m<sup>2</sup>/g or less as well as less than half of the specific surface area of a nucleus of carbon matter.

[0010] These inventions were not only extremely effective for enhancement of high rate charge and discharge characteristics and discharge characteristic at low temperature of the lithium ion secondary cell, but also effective for decreasing the irreversible capacity determined in the initial phase of cycle, which was a fatal problem to be solved. However, such problems are still left that storage property and reliability when left at a high temperature are not sufficiently achieved, and the specific capacity (mAh/g) and capacity density (mAh/cc) of the negative electrode are not satisfactory.

[0011] It is thus an object of the invention to improve further the reliability and high energy density of a lithium secondary cell.

#### DISCLOSURE OF INVENTION

[0012] To solve the aforesaid problems of the lithium ion secondary cell, according to the present invention, a carbonaceous powder of plural-layer structure with a surface layer of carbonaceous matter formed therein is used as a negative electrode material, said carbonaceous powder being prepared such that, using a lumpy graphite powder as a nucleus, this nucleus or the graphite powder is covered with a carbon precursor, which is then fired in an inert gas atmosphere at a temperature within the range of 700 to 2800°C, thereby causing the surface layer of the carbonaceous matter to form, wherein said lumpy graphite powder has the following characteristics:

- (1) the plane interval (d002) of (002) plane by wide angle X-ray diffraction method is less than 3.37 angstroms, and the size (L<sub>c</sub>) of crystallite in a C-axis direction is at least 1000 angstroms or more,
  - (2) R value, that is the peak intensity ratio of 1360 cm<sup>-1</sup> in relation to the peak intensity of 1580 cm<sup>-1</sup> in the argon ion laser Raman spectrum, is 0.3 or less, and the half width of 1580 cm<sup>-1</sup> peak is 24 cm<sup>-1</sup> or less,
  - (3) the mean particle size is 10 to 30 microns, and the thickness of the thinnest portion is at least 3 microns or more and not exceeding the mean particle size,
  - (4) the specific surface area by BET method is 3.5 m<sup>2</sup>/g or more and not exceeding 10.0 m<sup>2</sup>/g,
  - (5) the tapping density is 0.5 g/cc or more and not exceeding 1.0 g/cc, and
  - (6) the X-ray diffraction peak intensity ratio of (110)/(004) by wide angle X-ray diffraction method is 0.015 or more;
- whereby a nonaqueous electrolyte secondary cell of high specific capacity is realized, wherein the irreversible capacity noted in the initial cycle is made as small as possible, the storage property and reliability of the battery when left at a high temperature are enhanced, and excellent high rate discharge characteristic and discharge characteristic at a low temperature are achieved.

#### BRIEF DESCRIPTION OF DRAWINGS

##### [0013]

Fig. 1 is a sectional view of a coin type cell for measuring the reversible capacity and irreversible capacity for studying the effects achieved by the present invention; and  
Fig. 2 is a sectional view of a cylindrical cell in a vortex electrode group constitution according to an embodiment of the present invention.

## BEST MODES FOR CARRYING OUT THE INVENTION

[0014] The present invention as set forth in claim 1 relates to a nonaqueous electrolyte secondary cell comprising a positive electrode, a negative electrode, and a separator interposed therebetween, said negative electrode being made of a negative electrode material which allows lithium ions to repeat intercalation and deintercalation reversibly by charge and discharge, wherein a carbonaceous powder of plural-layer structure with a surface layer of carbonaceous matter formed therein is used in said negative electrode material, said carbonaceous powder being prepared such that, using a lumpy graphite powder as a nucleus, a surface of this nucleus or the graphite powder is covered with a carbon precursor, which is then fired in an inert gas atmosphere at a temperature within the range of 700 to 2800°C, thereby causing the surface layer of carbonaceous matter to form, wherein said lumpy graphite powder has the following characteristics:

- (1) the plane interval (d002) of (002) plane by wide angle X-ray diffraction method is less than 3.37 angstroms, and the size (Lc) of crystallite in a C-axis direction is at least 1000 angstroms or more,
- (2) R value, that is the peak intensity ratio of  $1360\text{ cm}^{-1}$  in relation to the peak intensity of  $1580\text{ cm}^{-1}$  in the argon ion laser Raman spectrum, is 0.3 or less, and the half width of  $1580\text{ cm}^{-1}$  peak is  $24\text{ cm}^{-1}$  or less,
- (3) the mean particle size is 10 to 30 microns, and the thickness of the thinnest portion is at least 3 microns or more and not exceeding the mean particle size,
- (4) the specific surface area by BET method is  $3.5\text{ m}^2/\text{g}$  or more and not exceeding  $10.0\text{ m}^2/\text{g}$ ,
- (5) the tapping density is  $0.5\text{ g/cc}$  or more and not exceeding  $1.0\text{ g/cc}$ , and
- (6) the X-ray diffraction peak intensity ratio of (110)/(004) by wide angle X-ray diffraction method is 0.015 or more, whereby characteristics of the lithium ion secondary cell are improved, and a high energy density is achieved.

[0015] The lumpy graphite particles having the above characteristics (1) to (6) are composed of natural or artificial scaly or flaky graphite of high purity and high crystallinity, and prepared by the process of grinding the graphite particles for chamfering or splintering them, or grinding them into spherical form, followed by a sifting process, and by collecting the graphite particles that are large in the thickness, that is, those that are approximately spherical form among flaky particles, by which particles with a tapping density of 0.5 or more can be obtained without unnecessarily increasing the specific surface area. Preferably, at this time, the X-ray diffraction peak intensity ratio of (110)/(004) by wide angle X-ray diffraction method should be 0.015 or more, and the shape factor should be spherical, with a mean roundness (the ratio of the peripheral length of a circle corresponding to the particle area as the numerator to the peripheral length of the projected particle image as the denominator, which becomes closer to 1 when the particle image is closer to true roundness, and becomes smaller as the particle image is slender or rugged) of 0.940 or more. By way of example, a method of sifting graphite particles after grinding and chamfering them into disk or tablet form particles in the process of further pulverizing the flaky graphite particles by a fluid energy grinder may be proposed, but the method of preparation is not particularly limited as long as the graphite particles having the characteristics (1) to (6) are obtained.

[0016] The mean particle size of the graphite powder is preferably 10 to 30 microns, more preferably 12 to 26 microns, and most preferably 15 to 23 microns. It is further preferred that the content of the powder with a particle size of less than 10 microns is 20% or less, preferably 10% or less, or alternatively the content of the powder with a particle size exceeding 25 microns is 20% or less, preferably 10% or less. It is most preferred that the respective contents of the powder with a particle size of less than 10 microns and the powder with a particle size of more than 25 microns are both 20% or less, preferably 10% or less and 20% or less, respectively, or most preferably both 10% or less. The powder of which specific surface area by BET method is within a range of  $3.5$  to  $10.0\text{ m}^2/\text{g}$  may be used, but it should preferably be  $4.0$  to  $8.0\text{ m}^2/\text{g}$ , and most preferably  $4.0$  to  $7.0\text{ m}^2/\text{g}$ .

[0017] The theoretical value of capacity per 1 g of carbon by reference to  $\text{C}_6\text{Li}$  of interlayer compound produced by intercalation of lithium ion is 372 mAh, and the graphite particles that have thus been selected should preferably have a specific capacity of 330 mAh/g or more, more preferably 350 mAh/g or more, according to measurement of electric capacity using a half cell having lithium metal pair electrodes with the charge and discharge rate at  $0.2\text{ mA/cm}^2$ , that is, the closer its specific capacity is to the above theoretical capacity, the more preferably such graphite powder will be used.

[0018] The carbon precursor for covering the surface of graphite particle nucleus usable in the present invention includes, as an organic matter which promotes carbon forming in liquid phase, coal derivative heavy oil such as coal tar pitch from soft pitch to hard pitch and coal liquefied oil, petroleum derivative heavy oil including straight heavy oil such as asphaltene, and cracked heavy oil such as naphtha tar obtained as byproduct of thermal cracking of crude oil or naphtha, and heat treatment pitch such as ethylene tar pitch, FCC decanted oil and Ashland pitch obtained by heat treatment of cracked heavy oil. Further examples include vinyl derivative high polymer such as polyvinyl chloride, polyvinyl acetate, polyvinyl butyral and polyvinyl alcohol, substitution phenol resin such as 3-methyl phenol formaldehyde resin and 3,5-dimethyl phenol formaldehyde resin, aromatic hydrocarbon such as asenaphthylene, decacyclene and

anthracene, nitrogen cyclic compound such as phenadine and acrydine, and sulfur cyclic compound such as thiophene. Also, as an organic matter which promotes carbon forming in solid phase, natural high polymer such as cellulose, chain vinyl resin such as polyvinylidene chloride and polyacrylonitrile, aromatic polymer such as polyphenylene, thermosetting resin such as furfuryl alcohol resin, phenol formaldehyde resin and imide resin, and thermosetting resin material such as furfuryl alcohol may be used. These organic matters may be used and applied on the surface of graphite particle nucleus as required, by dissolving and diluting them in a proper solvent.

[0019] In the present invention, normally, the mixture of such graphite particle nucleus and carbon precursor is heated to obtain an intermediate substance, which is then carbonized, fired, and ground, thereby finally obtaining a carbonaceous powder of plural-layer structure in which a surface layer of carbonaceous matter is formed on the surface of the graphite particle nucleus, wherein the rate of the carbonaceous matter in the carbonaceous powder of plural-layer structure is adjusted to be 0.1 wt% or more and not exceeding 50 wt%, preferably 0.5 wt% or more and not exceeding 25 wt%, even more preferably 1 wt% or more and not exceeding 15 wt%, and most preferably 2 wt% or more and not exceeding 10 wt%.

[0020] Meanwhile, the manufacturing process for obtaining such plural-layer carbonaceous matter of the present invention can be divided into the following four steps.

First step:

[0021] A step of obtaining a mixture of graphite particles, a carbon precursor, and, if necessary, a solvent, by mixing them with the use of various commercial mixing machines or kneading machines.

Second step:

[0022] A step of obtaining an intermediate substance by heating the above said mixture while stirring same as required, thereby removing the solvent.

Third step:

[0023] A step of obtaining a carbonaceous substance by heating the above said mixture or intermediate substance in an inert gas atmosphere such as nitrogen gas, carbon dioxide, or argon gas, at a temperature of 700°C or more and 2800°C or less.

Fourth step:

[0024] A step of processing the above said carbonaceous substance into a powder, by grinding, crushing, sorting or other processing, as required.

[0025] Of these steps, the second and fourth steps can be omitted depending on cases, and the fourth step may be carried out before the third step.

[0026] Further, as the heating treatment condition in the third step, the thermal history temperature condition is essential. The lower limit temperature varies depending on the type of the carbon precursor and its thermal history, but it is normally 700°C or more, and preferably 900°C or more. On the other hand, the upper limit temperature can be basically raised to a temperature at which the structural order of the carbon precursor does not exceed the crystal structure of the graphite particle nucleus. Therefore, the upper limit temperature of heat treatment is usually 2800°C or less, preferably 2000°C or less, or more preferably 1500°C or less. Under such heating treatment condition, the heating speed, cooling speed, and heat treatment duration can be freely set depending on purposes. It is also possible to increase the temperature to a predetermined temperature after conducting heat treatment in a relatively low temperature region. The reaction machine used in the process may be of either batch type or continuous type, and either one or plural units may be used.

[0027] In the carbonaceous powder material of plural-layer structure of the present invention thus forming therein the surface layer of carbonaceous matter, the peak intensity ratio or the R value by Raman spectrum analysis, and the values of d002 and Lc obtained in the diffraction diagram of X-ray wide angle diffraction are preferred not to exceed the degree of crystallinity of the graphite material forming the nucleus; that is, the R value should be more than that of the nucleus, the half width  $\Delta v$  should be more than that of the nucleus, the d002 value should be more than that of the nucleus, and the Lc should not exceed that of the nucleus. To be concrete, the R value of the carbonaceous powder material of plural-layer structure should be 0.01 or more and not exceeding 1.0, preferably 0.05 or more and not exceeding 0.8, more preferably 0.1 or more and not exceeding 0.6, and even more preferably 0.2 or more and not exceeding 0.4, and also more than that of the nucleus. The mean particle size is preferred to be 11 to 40 microns, and more preferably 13 to 30 microns, and most preferably 16 to 25 microns. Even more preferably, the content of a powder with a

particle size of less than 10 microns should be 20% or less, preferably 10% or less, or the content of a powder with a particle size exceeding 25 microns should be 20% or less, preferably 10% or less. Moreover, the contents of a powder with a particle size of less than 10 microns and a powder with a particle size exceeding 25 microns should preferably be both 20% or less, more preferably 10% or less and 20% or less, respectively, and most preferably both 10% or less.

5 The mean value of the thickness of the thinnest portion of particle should be 4 microns or more and not exceeding the mean particle size. Further, the specific surface area by BET method should be 1.0 to 5.0 m<sup>2</sup>/g, more preferably 1.5 to 4.0 m<sup>2</sup>/g, and even more preferably 2.0 to 3.5 m<sup>2</sup>/g. Although the tapping density of the carbonaceous powder material of plural-layer structure is further increased as compared with that of the graphite material used as the nucleus owing to carbon coating, it is preferred to be controlled within a range of 0.7 to 1.2 g/cc. The carbonaceous powder defined  
10 within such ranges is mixed with a binder and other additives, which is coated or pressed on a current collector made of copper, nickel or the like, so as to be used as an electrode. Then, the density of the active material layer on the electrode (hereinafter referred to as plate density) is adjusted by a rolling process with a flat press or a roll press. At this time, by setting the plate density more than 1.2 and less than 1.6, preferably 1.3 or more and not exceeding 1.5, the capacity per unit volume of battery can be obtained to the maximum extent without lowering the battery capacity in low  
15 temperature discharge or high rate discharge. In a battery that is constituted by combining a thus formed negative electrode and an ordinary positive electrode of metal chalcogenide derivative for lithium ion cell, a high voltage of 4V class is realized, the capacity is large, the irreversible capacity recognized in the initial cycle is small, the storage property and reliability of battery when left at a high temperature are increased, and the high rate discharge characteristic and discharge characteristic at low temperature are extremely excellent. In this case, the chalcogenide derivative positive electrode is preferably Li<sub>x</sub>MO<sub>2</sub> (M is one or more transition metal, x = 0 to 1.2), and, in particular, Li<sub>x</sub>CoO<sub>2</sub>, Li<sub>x</sub>NiO<sub>2</sub>,  
20 Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>, and those having part of Co, Ni, Mn replaced with an element of other transition metal or the like.

[0028] In the present invention, the electrolyte solution is not particularly limited to a specific type, but the solvent of the electrolyte solution used in the battery composed of the aforesaid 4V class positive electrode and the negative electrode of the present invention is preferred to be mainly composed of a mixed solvent of one kind or more of cyclic carbonate such as ethylene carbonate, propylene carbonate and butylene carbonate that are excellent in oxidation  
25 resistance and low temperature characteristic, and one kind or more of chain carbonate such as dimethyl carbonate, diethyl carbonate and ethyl methyl carbonate. Other solvents, such as aliphatic ester carboxylate or ethers may be also mixed as required. The mixing ratio by volume of cyclic carbonate and of chain carbonate in relation to the entire solvent should be within the range of 5 to 50% and 10 to 90%, respectively, and more preferably 15 to 40% and 20 to 80%,  
30 respectively.

[0029] Incidentally, in case of using a material of relatively low potential of 3 V class or the like for the positive electrode, solvents other than those mentioned above may be also used.

[0030] Lithium salt is used as the solute for such solvents. Well-known examples of lithium salt include LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiAlCl<sub>4</sub>, LiSbF<sub>6</sub>, LiSCN, LiCl, LiCF<sub>3</sub>SO<sub>3</sub>, LiCF<sub>3</sub>CO<sub>2</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiAsF<sub>6</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, etc.

35 [0031] No restrictions are placed on selection of members necessary for constituting the battery other than those mentioned above.

[0032] The battery using the above carbonaceous powder material of plural-layer structure with a surface layer of carbonaceous matter formed therein as the negative electrode exhibits enhanced high rate charge and discharge performances and high rate discharge performance at low temperature, as compared with the battery using, as the negative  
40 electrode, graphite particles on which is not formed a surface layer of carbonaceous matter, or a carbonaceous powder material of plural-layer structure with a surface layer of carbonaceous matter formed therein using graphite particles that do not have the above characteristics (1) to (6). Moreover, since the organic solvent in the electrolyte is hardly decomposed even at a high temperature, and the internal pressure of the cell is hardly raised, the conventional problem of leakage accident of electrolyte can be prevented. In addition, the use of the carbonaceous powder of plural-layer  
45 structure allows the specific surface area to remain small, thus the organic solvent in the electrolyte is hardly decomposed even at a high temperature, and deterioration of cell performance at the high temperature can be suppressed.

(Embodiments)

50 [0033] Referring now to the drawings and tables, preferred embodiments of the present invention will be hereinafter described in detail.

(Measuring methods)

55 (1) Mean particle size by reference to volume

[0034] About 1 cc of 2 vol% aqueous solution of polyoxyethylene (20) sorbitan monolaurate was premixed as a surface active agent in the carbonaceous powder, and then using ion exchange water as a dispersant, the mean particle

size by reference to volume (median diameter) was measured by means of laser diffraction type particle size distribution meter LA-700 of Horiba.

(2) Tapping density

[0035] Using a sieve of 300-micron opening size for passing samples, the powder was dropped in a 20cc tapping cell until it is filled up, tapping was repeated with a stroke length of 10 mm by 1000 times, and the tapping density was measured by means of powder density measuring instrument Tap Denser KYT-3000 of Seishin Kigyosha.

(3) Measurement of specific surface area by BET

[0036] After heating to 350°C as preliminary drying and passing nitrogen gas for 15 minutes, the specific surface area was measured by BET one-point method at relative pressure of 0.3 by nitrogen gas adsorption using AMS-8000 of Okura Riken.

(4) X-ray diffraction

[0037] An X-ray standard high purity silicon powder of about 15% in relation to the sample was admixed in the sample, with which the sample cell was filled up, and wide angle X-ray diffraction curve was measured by reflection type diffractometer method, using CuK $\alpha$  ray made monochromatic by graphite monochromator as the source. From the wide angle X-ray diffraction curve obtained by the measurement, the plane interval (d002) of (002) plane and crystallite size (Lc) in the C-axis direction were measured according to the method recommended by Japan Society for the Promotion of Science.

(5) Raman measurement

[0038] In Raman spectrum analysis using argon ion laser beam with wavelength of 514.5 nm, intensity IA of peak PA near 1580 cm<sup>-1</sup>, and intensity IB of peak PB in a range of 1360 cm<sup>-1</sup> were measured, using NR-1800 of Nippon Bunko, and the intensity ratio R = IB/IA was calculated. At the same time, the half width of the peak PA near 1580 cm<sup>-1</sup> was determined in the unit of wave number (cm<sup>-1</sup>). In preparation of the samples, the powder was naturally dropped to fill up the cell, and measurement was made while a laser beam is emitted to the sample surface in the cell and the cell was rotated within a plane vertical to the laser beam.

(6) Mean thickness of thinnest portion of carbon powder

[0039] Each of the sample graphite powder materials was pressed and formed using a die, and the formed materials were cut in parallel to the pressing direction. The mean thickness of carbon powder was determined from an SEM image of this sectional plane of the formed materials. Specifically, the value of the thinnest portion of carbon powder in the thickness direction was measured in more than 100 pieces, and the mean was determined.

(7) Measurement of X-ray peak intensity ratio of (110)/(004)

[0040] The X-ray peak intensity ratio of (110)/(004) was obtained such that the carbon powder was pressed with a die to form pellets of density of about 1.7 g/cc, the peak intensity ratio of (110)/(004) obtained by wide angle X-ray diffraction measurement was calculated, and the mean was determined. Diffraction beams on the (004) plane and (110) plane are diffraction beams on six-carbon ring reticular plane and its vertical plane of graphite crystal. When there are many particles of flaky shape, graphite particles are oriented selectively in the direction parallel to the pressing plane when they are formed into pellets, as compared with cases when there are many graphite particles of disk or tablet shape. Therefore, when the ratio of flaky particles increases in relation to the disk or tablet-like graphite particles, the X-ray peak intensity ratio of (110)/(004) decreases.

(8) Measurement of mean roundness

[0041] Using flow type particle image analyzer FPIA-1000 of Toa Medical Electronics, images of graphite particles dispersed in water were taken by a CCD camera in every 1/30 second, and the particle images were analyzed in real time, by which the mean roundness of all particles was calculated. The dispersant was ion exchange water, and the surface active agent was polyoxyethylene (20) sorbitan monolaurate. The mean roundness is the ratio of the peripheral length of a circle corresponding to the area of a projected particle image as the numerator to the peripheral length of

the projected particle image as the denominator, and it becomes closer to 1 when the particle image is closer to true roundness, and the value becomes smaller as the particle image is slender or rugged.

(Basic experiment 1)

[0042] Fig. 1 is a sectional view of a coin type cell for measuring the reversible capacity and irreversible capacity of the negative electrode of a lithium ion secondary cell. In Fig. 1, a grid 3 of stainless steel expanded metal is preliminarily spot-welded to the inner bottom of a stainless steel cell case 1, and this grid 3 and a compound mainly composed of the carbon powder for negative electrode of lithium ion secondary cell are integrally fixed as a carbon electrode 5 by an internal forming method. The compound of the carbon electrode 5 is a mixture of a sample carbon powder and an acrylic binder at a ratio of 100:5 by weight. A polypropylene gasket 7 is fitted to the brim of a stainless steel lid 2, and metal lithium 4 is pressed to the inner surface of the lid 2. After injecting and impregnating nonaqueous electrolyte to the carbon electrode 5, the lid 2 with the gasket 7 is coupled to the cell case 1 through a separator 6 of micro-porous polyethylene film, and the upper edge opening of the cell case 1 is curled inwardly and sealed. As the nonaqueous electrolyte, an organic electrode prepared by mixing ethylene carbonate and diethyl carbonate at a ratio of 1:1 by volume, and dissolving lithium hexafluorophosphate in this mixed solvent at a concentration of 1 mol/liter was employed. Cells were fabricated using 14 kinds of sample carbon powder in the carbon electrode 5, and using the carbon electrode 5 as the positive electrode and the metal lithium electrode 4 as the negative electrode, charging and discharging were repeated at constant current of current density of  $0.3 \text{ mA/cm}^2$  at  $20^\circ\text{C}$ . After intercalating lithium in carbon until the cell voltage becomes 0 V, lithium is deintercalated from carbon until the cell voltage is 1.0 V, and the determined capacity is the reversible capacity. By subtracting the reversible capacity from the quantity of electricity required for intercalation, the irreversible capacity is obtained. The charge and discharge end voltages of these test cells nearly correspond to the charge end voltage of 4.20 V and discharge end voltage of 2.75 V of a commercial cell of carbon negative electrode and  $\text{LiCoO}_2$  positive electrode.

[0043] Flaky artificial and natural graphite powder obtained by a conventional grinding method, artificial and natural graphite powder of which tapping density has been enhanced by various grinding methods (sample Nos. 1 to 15), and as comparative samples, spherical meso-carbon micro-beads (MCMB, sample No. 16) that are obtained by graphitizing meso-carbon micro-beads as disclosed in Japanese Laid-open Patent No. 7-134988, and petroleum pitch coke powder (sample No. 17) are prepared as sample carbon powder materials for negative electrode, properties of these sample powder materials and the reversible capacity and irreversible capacity mentioned above are summarized in Table 1.



[Table 1]

Sam- ple No.	Material	Manu- facturer	Trade- name	Powder properties							Electric characteristics				
				d002 (Å)	Lc (Å)	Raman R value	Raman half width (cm <sup>-1</sup> )	Mean particle size (μm)	Specific surface area (m <sup>2</sup> /g)	Mean thickness of thin- nest portion (μm)	Tapping density (g/cc)	Mean round- ness	(110/ 004)	Revers- ible capacity (mAh/g)	Irrevers- ible capacity (mAh/g)
1	Artificial graphite	Timcal	KS15	3.36	1000 or more	0.16	21.1	7.8	14.5	1.1	0.32	0.928	0.008	351	53
2	Artificial graphite	Timcal	KS25	3.36	1000 or more	0.16	21.4	10.1	11.9	1.3	0.40	0.925	0.009	353	43
3	Artificial graphite	Timcal	KS44	3.36	1000 or more	0.15	22.2	18.8	9.3	1.8	0.41	0.919	0.010	359	36
4	Artificial graphite	Timcal	KS75	3.36	1000 or more	0.15	22.2	23.7	7.2	2.1	0.44	0.918	0.011	353	35
5	Artificial graphite	Nippon graphite	SP-10	3.35	1000 or more	0.18	21.2	32.5	6.9	2.4	0.41	0.927	0.012	353	32
6	Artificial graphite	Nippon graphite	SP-20	3.36	1000 or more	0.15	24.0	14.9	8.7	1.8	0.23	0.937	0.010	356	40
7	Natural graphite	SEC	SNO10	3.35	1000 or more	0.19	20.9	10.4	8.7	2.0	0.46	0.919	0.008	362	39
8	Natural graphite	SEC	SNO15	3.35	1000 or more	0.17	21.5	12.9	7.8	2.3	0.46	0.927	0.009	361	35
9	Natural graphite	SEC	SNO20	3.36	1000 or more	0.16	21.6	18.7	6.8	2.5	0.48	0.930	0.008	358	34
10	Natural graphite	Nippon graphite	ACP- 20NB	3.36	1000 or more	0.18	21.6	19.0	4.9	5.4	0.64	0.947	0.038	354	23
11	Natural graphite	Nippon graphite	ASP- 20NB	3.36	1000 or more	0.17	21.1	16.7	4.9	6.3	0.66	0.943	0.039	357	20
12	Artificial graphite	Nippon graphite	SP-20NB	3.36	1000 or more	0.20	20.9	15.7	6.6	3.5	0.61	0.942	0.032	360	26
13	Natural graphite	Chuetsu graphite	H-0	3.36	1000 or more	0.21	22.0	22.3	5.6	5.6	0.65	0.940	0.035	358	24
14	Natural graphite	Chuetsu graphite	H-1	3.36	1000 or more	0.18	21.8	18.4	5.8	6.5	0.79	0.941	0.038	355	24
15	Natural graphite	Chuetsu graphite	H-2	3.36	1000 or more	0.24	22.1	17.7	6.4	5.8	0.70	0.940	0.039	356	26
16	Artificial graphite	Osaka Gas	MCMB	3.37	700	0.19	25.4	5.3	2.9	5.3	1.10	0.966	0.120	295	18
17	Artificial graphite	Nippon graphite	GMW- 20NB	3.37	750	0.32	25.0	17.2	5.3	8.1	0.95	0.961	0.110	288	27

[0044] As can be seen from Table 1, the cells with the spherical graphite powder (sample No. 16) and the coke powder (sample No. 17) in comparative samples with Lc of less than 1000 angstroms had relatively small irreversible capacities,

but the reversible capacities which greatly influence the energy density were small (both less than 300 mAh/g). In contrast, all of the cells with the sample Nos. 1 to 15 made of natural graphite or artificial graphite powder had the reversible capacity of at least 350 mAh/g, which was close to the theoretical value of specific capacity (372 mAh/g). Among them, it is noted that the irreversible capacities of the cells with the sample graphite powder Nos. 10 to 15 are 20 to 26 mAh/g, that are smaller as compared to those of the cells with other sample graphite powder (Nos. 1 to 9).

[0045] It is understood that a high level reversible capacity is obtained by using natural graphite or artificial graphite of high degree of crystallinity and purity with the plane interval (d002) of (002) plane being less than 3.37 angstroms by wide angle X-ray diffraction and the crystallite size (Lc) in the C-axis direction being at least 1000 angstroms or more, in the negative electrode material of lithium ion secondary cell, as the preliminary conditions of the present invention.

(Basic experiment 2)

[0046] Using the same carbon powder materials for negative electrode (sample Nos. 1 to 17) of which reversible capacity and irreversible capacity were determined in the basic experiment 1, cylindrical cells were fabricated, and the high rate discharge characteristic at a low temperature and electrolyte leak possibility when left at a high temperature in a charged state were investigated.

[0047] Fig. 2 is a sectional view of a cylindrical cell of spiral electrode group configuration. In Fig. 2, a band-like positive electrode 10 and a negative electrode 11 are spirally wound with a separator 12 made of micro-porous polyethylene film interposed therebetween, thereby constituting an electrode group. The positive electrode 10 is prepared by mixing  $\text{LiCoO}_2$  which is a composite oxide of lithium and cobalt of active materials, carbon black as conductive material, and polytetrafluoroethylene (PTFE) as a binder at a ratio of 100:3:10 by weight, applying this paste on both sides of an aluminum foil used as a current collector, drying and pressing it by a roll, and cutting it to a prescribed size. A dispersion solution was used for the PTFE as the binder. A positive electrode lead piece 13 is spot-welded to the aluminum foil of the positive electrode 10. The negative electrode 11 is prepared by applying a paste, that is obtained by admixing an acrylic binder solution into the sample carbon powder, on both sides of a copper foil used as a current collector, drying and pressing it by a roll, and cutting it to a specified size. A negative electrode lead piece 14 is spot-welded to the copper foil of the negative electrode 11. A bottom insulator 15 is mounted on the lower side of the wound electrode group, which is then put into a cell case 16 made of a nickel plated steel plate, and the negative electrode lead piece 14 is spot-welded to the inner bottom of the cell case 16. Then, after placing an upper insulator 17 on the electrode group, a groove is cut in a prescribed position at the opening of the cell case 16, and a predetermined amount of organic electrolyte is injected therein and impregnated. As the organic electrolyte, the same kind as used in the basic experiment 1 was used. Afterwards, the positive electrode lead piece 13 is spot-welded to the inner bottom of a seal plate 19 to which a gasket 18 has been fitted at its peripheral edge. The seal plate 19 is then fitted to the opening of the cell case 16 through the gasket 18, and the upper edge of the cell case 16 is curled inwardly and sealed, thereby completing a cell.

[0048] The discharge capacity of each cell was set such as to be defined by the negative electrode capacity, and the weight of carbon powder for negative electrode of each cell was made identical regardless of the kind. The amount of other materials and manufacturing method were made identical, so that the comparison could be made with respect to the carbon powder materials for negative electrode.

[0049] All the cells, five cells each for cells A to Q, that are respectively made of 17 kinds of carbon powder for negative electrode, were charged at 20°C at a constant current of 100 mA (1/5C) until the terminal voltage of each cell became 4.2 V, after which they were discharged at a constant current of 100 mA (1/5C) until 2.75V, and the 1/5C discharge capacity was determined. Then, after charging the cells in a similar manner, they were discharged at a constant current of 500 mA (1C) until 2.75V, and the 1C discharge capacity was determined. Successively, the cells were charged at 20°C, after which they were left at -20°C for 24 hours, and the 1C discharge capacity was determined at the same temperature of -20°C. Further, after letting each of the cells stand at 20°C, when the temperature of the cells had returned to 20°C, they were charged in a similar manner, and then the cells were left at 100°C for one day, and after the cell temperature had returned to 20°C, all cells were observed for presence or absence of electrolyte leak.

[0050] The above mentioned battery performances (mean of five cells) are summarized in Table 2 in contrast to the properties of the sample carbon powder.

[Table 2]

Sample No.	Material	Manufacturer	Tradename	Cell symbol	Battery performance			
					1/5C Discharge capacity	1C Discharge capacity	-20°C 1C Discharge capacity	Number of electrolyte leak after being left at high temperature
1	Artificial graphite	Timcal	KS15	A	511	501	450	5/5
2	Artificial graphite	Timcal	KS25	B	532	523	452	3/5
3	Artificial graphite	Timcal	KS44	C	539	521	410	2/5
4	Artificial graphite	Timcal	KS75	D	549	508	357	0/5
5	Artificial graphite	Nippon graphite	SP-10	E	537	483	267	1/5
6	Artificial graphite	Nippon graphite	SP-20	F	541	528	433	2/5
7	Natural graphite	SEC	SNO10	G	538	522	473	3/5
8	Natural graphite	SEC	SNO15	H	545	531	452	2/5
9	Natural graphite	SEC	SNO20	I	536	520	407	1/5
10	Natural graphite	Nippon graphite	ACP-20NB	J	554	543	421	0/5
11	Natural graphite	Nippon graphite	ASP-20NB	K	561	550	445	0/5
12	Artificial graphite	Nippon graphite	SP-20NB	L	557	546	440	0/5
13	Natural graphite	Chuetsu graphite	H-0	M	553	541	420	0/5
14	Natural graphite	Chuetsu graphite	H-1	N	554	545	440	0/5
15	Natural graphite	Chuetsu graphite	H-2	O	560	548	445	0/5
16	Artificial graphite	Osaka gas	MCMB	P	478	463	417	0/5
17	Artificial graphite	Nippon graphite	GMW-20NB	Q	483	468	372	0/5

[0051] As can be seen from Table 2, the cells with sample Nos. 16 and 17 which had small reversible capacities as shown in Table 1, have small 1/5C and 1C discharge capacities at 20°C, while those of the cells with sample graphite

powder Nos. 1 to 15 are relatively large. However, of sample Nos. 1 to 15, those which exhibited high rate discharge capacities at low temperature (-20°C, 1C) of 400 mA or more were cells A, B, C, F, G, H, I, J, K, L, M, N, and O, that were respectively made of the sample graphite powder Nos. 1, 2, 3, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. Further, those which were completely free from electrolyte leak after being left at a high temperature were the cells D, J, K, L, M, N, O, P, and Q, that were respectively made of the sample graphite powder Nos. 4, 10, 11, 12, 13, 14, 15, 16 and 17. From these results, it is seen that those which were excellent in all aspects of battery performances were the cells J, K, L, M, N and O, that were respectively made of the sample graphite powder Nos. 10, 11, 12, 13, 14, and 15.

(Embodiments and comparative examples)

[0052] Among the cells of which 1/5C discharge capacity, 1C discharge capacity, 1C discharge capacity at -20°C, and electrolyte leak possibility after being left at a high temperature were measured in the basic experiment 2, the cells J, K, L, M, N and O respectively made of sample graphite powder Nos. 10, 11, 12, 13, 14, and 15, that were excellent in all aspects of battery performances, were left at a high temperature, after which their respective 1/5C discharge capacities at 20°C were determined under the same charge and discharge conditions as those described with respect to the basic experiment 2, and the result was such that they exhibited only 70 to 80% of the 1/5C discharge capacity as compared to that before being left at a high temperature. These cells were completely free from electrolyte leak accident when left at the high temperature, and thus on one hand the reliability of the cells was enhanced but on the other hand deterioration of battery characteristics was significant, wherefore it is necessary to minimize the deterioration of battery characteristics even in the cases where they are left at high temperatures.

[0053] Accordingly, using the carbon powder materials for negative electrode (sample Nos. 1 to 17) with which battery performances were measured in the basic experiment 2 as the nucleus, these carbon powder materials were coated with petroleum tar pitch obtained from naphtha cracking as a carbon precursor such as to be 5 wt% after carbonization, and heated finally at 1200°C in an inert gas flow. Then, after being cooled to a room temperature, the carbon powder materials were crushed with a grinder to obtain carbon composite powders with a specific particle size distribution. The carbonaceous powder (sample Nos. 18 to 34) of plural-layer structure, with a new surface layer of carbonaceous matter that has been formed on the surface of its nucleus, was thus prepared, and used as the sample carbon powder for negative electrode.

[0054] Five cells each for cells R to AH were respectively fabricated in a similar manner as in the basic experiment 2, except 17 kinds of carbon powder for negative electrode were used, the same battery performances were measured, and in addition, the 1/5C discharge capacities of the cells that were free from electrolyte leak after being left at a high temperature were measured.

[0055] The battery performances mentioned above are summarized in Table 3 in contrast with the properties of the sample carbon powder.

Table 3]

Sample No.	Nucleus sample No.	Material	Manu- facturer	Trade- name	Powder properties				Cell sym- bol	Battery performance					
					Mean particle size (μm)	Specific surface area (m <sup>2</sup> /g)	Mean thick- ness of thin- nest portion (μm)	Tapping density (g/cc)		1/5C Discharge capacity (mAh)	1C Discharge capacity (mAh)	-20°C 1C Discharge capacity (mAh)	Number of electrolyte leak after being left at high temperature	1/5C Discharge capacity after being left at high temperature (mAh)	1/5C Discharge capacity ratio before and after being left at high temperature (%)
18	1	Artificial graphite	Timcal	KS15	12.0	4.9	1.9	0.47	R	520	513	448	4/5	-	-
19	2	ditto	ditto	KS25	12.4	4.5	2.4	0.57	S	542	530	454	2/5	-	-
20	3	ditto	ditto	KS44	17.7	4.2	2.6	0.61	T	549	532	411	1/5	-	-
21	4	ditto	ditto	KS75	23.2	3.1	3.1	0.74	U	553	520	357	0/5	455	82.3
22	5	ditto	Nippon graphite	SP-10	38.8	2.5	3.3	0.62	V	547	490	269	1/5	-	-
23	6	ditto	ditto	SP-20	22.9	4.8	2.7	0.57	W	549	535	434	2/5	-	-
24	7	Natural graphite	SEC	SNO10	18.6	4.1	3.1	0.82	X	541	530	475	2/5	-	-
25	8	ditto	ditto	SNO15	21.4	3.7	3.2	0.81	Y	554	537	452	1/5	-	-
26	9	ditto	ditto	SNO20	25.2	2.9	3.4	0.83	Z	542	528	409	1/5	-	-
27	10	ditto	Nippon graphite	ACP-20NB	20.2	2.6	8.1	0.81	AA	566	552	423	0/5	531	93.8
28	11	ditto	ditto	ASP-20NB	21.4	2.8	10.2	0.88	AB	569	559	447	0/5	534	93.8
29	12	Artificial graphite	ditto	SP-20NB	21.5	2.8	4.9	0.70	AC	567	549	443	0/5	532	93.8
30	13	Natural graphite	Chuetsu graphite	H-0	24.8	2.3	7.6	0.85	AD	560	550	425	0/5	530	94.6
31	14	ditto	ditto	H-1	24.0	2.4	10.5	0.94	AE	561	552	458	0/5	532	94.8
32	15	ditto	ditto	H-2	21.2	2.6	8.3	0.92	AF	563	557	462	0/5	537	95.4
33	16	Artificial graphite	Osaka gas	MCMB	6.5	1.8	6.1	1.26	AG	485	570	415	0/5	450	92.8
34	17	ditto	Nippon graphite	GMW-20NB	17.2	1.6	8.7	1.05	AH	487	473	374	0/5	452	92.8

[0056] As can be seen from Table 3, no changes were observed in 1/5C discharge capacity, 1C discharge capacity, and 1C discharge capacity at -20°C as a result of using carbonaceous powder of plural-layer structure. However, in cells

R, S, T, V, W, X, Y, and Z respectively made of sample carbonaceous powder of plural-layer structure (Nos. 18, 19, 20, 22, 23, 24, 25, and 26) of which nucleus is sample Nos. 1, 2, 3, 5, 6, 7, 8, and 9, respectively, in which electrolyte leak was found in the basic experiment 2, the number of leaks showed a tendency to decrease, although it was insufficient to prevent electrolyte leak completely. On the other hand, those that were completely free from electrolyte leak after being left at a high temperature were cells U, AA, AB, AC, AD, AE, AF, AG, and AH respectively made of sample carbonaceous powder of plural-layer structure Nos. 21, 27, 28, 29, 30, 31, 32, 33, and 34. In these cells, the 1/5C discharge capacity after being left at a high temperature was 82 to 96% of the 1/5C discharge capacity before being left at the high temperature, which means, the 1/5C discharge capacity after being left at a high temperature was enhanced by using the carbonaceous powder of plural-layer structure. Of these cells, in all of the cells AA, AB, AC, AD, AE, and AF respectively made of the sample carbonaceous powder of plural-layer structure Nos. 27, 28, 29, 30, 31, and 32, the 1/5C discharge capacities after being left at a high temperature were at least 530 mAh or more, that is 93% or more of the 1/5C discharge capacity before being left at the high temperature. It is concluded from these results that those that were excellent in all aspects of battery performances were cells AA, AB, AC, AD, AE, and AF respectively made of sample carbonaceous powder of plural-layer structure Nos. 27, 28, 29, 30, 31, and 32.

[0057] Incidentally, the baking temperature for obtaining the carbonaceous powder of plural-layer structure was 1300°C in the above embodiments, but similar powder properties were achieved in a temperature range of 700 to 2800°C, whereby same effects as in the present invention were confirmed. Also, the carbonaceous powder of plural-layer structure was prepared by mixing the nucleus material and the pitch so that the ratio by weight of the graphite powder used as the nucleus and the carbon matter newly forming a surface layer will be 95:5, but similar properties were obtained with this ratio by weight being within the range of 99:1 to 50:50, whereby same effects as those of the present invention were achieved.

[0058] In the above description of the present invention, explanation is made only with respect to the organic electrolyte as the nonaqueous electrolyte, which does not mean that this invention should not be applied to a secondary cell composed of polymer or other cation conductive solid electrolyte in the secondary cell.

## INDUSTRIAL APPLICABILITY

[0059] As set forth above, the graphite powder for negative electrode according to the present invention achieves the capacity of 354 to 360 mAh/g, that is, at least 95% (95.2 to 96.8%) of the theoretical value of specific capacity (372 mAh/g), while its irreversible capacity is as extremely small as 20 to 26 mAh/g, by which it contributes to enhancement of energy density. Moreover, not only exhibiting excellent high rate charge and discharge performances and low temperature high rate discharge performance, but also it presents a highly reliable lithium secondary cell which is free from electrolyte leakage accidents even left at a high temperature, wherefore it is useful in the fabrication of lithium secondary cells.

## Claims

1. A nonaqueous electrolyte secondary cell comprising a positive electrode, a negative electrode, and a separator interposed therebetween, said negative electrode being made of a negative electrode material that allows lithium ions to repeat intercalation and deintercalation reversibly by charge and discharge, in which a carbonaceous powder of plural-layer structure with a surface layer of carbonaceous matter formed therein is used in said negative electrode material, said carbonaceous powder being prepared such that, using a lumpy graphite powder as a nucleus, a surface of this nucleus or the graphite powder is covered with a carbon precursor, which is then fired in an inert gas atmosphere at a temperature within the range of 700 to 2800°C, thereby causing the surface layer of carbonaceous matter to form, wherein said lumpy graphite powder has the following characteristics:

- (1) the plane interval (d002) of (002) plane by wide angle X-ray diffraction method is less than 3.37 angstroms, and the size (Lc) of crystallite in a C-axis direction is at least 1000 angstroms or more,
- (2) R value, that is the ratio of the peak intensity of 1360  $\text{cm}^{-1}$  in relation to the peak intensity of 1580  $\text{cm}^{-1}$  in the argon ion laser Raman spectrum, is 0.3 or less, and the half width of 1580  $\text{cm}^{-1}$  peak is 24  $\text{cm}^{-1}$  or less,
- (3) the mean particle size is 10 to 30 microns, and the thickness of the thinnest portion is at least 3 microns or more and not exceeding the mean particle size,
- (4) the specific surface area by BET method is 3.5  $\text{m}^2/\text{g}$  or more and not exceeding 10.0  $\text{m}^2/\text{g}$ ,
- (5) the tapping density is 0.5 g/cc or more and not exceeding 1.0 g/cc, and
- (6) the X-ray diffraction peak intensity ratio of (110)/(004) by wide angle X-ray diffraction method is 0.015 or more.

2. The nonaqueous electrolyte secondary cell according to claim 1, wherein a mean roundness of the graphite powder

der used as the nucleus is 0.940 or more.

3. The nonaqueous electrolyte secondary cell according to claim 1, wherein a tapping density of the carbonaceous powder of plural-layer structure is 0.7 g/cc or more and not exceeding 1.2 g/cc.

4. The nonaqueous electrolyte secondary cell according to claim 1, wherein a specific surface area of the carbonaceous powder of plural-layer structure by BET method is 1.0 to 5.0 m<sup>2</sup>/g.

5. The nonaqueous electrolyte secondary cell according to claim 1 or 2, wherein a mean particle size of the carbonaceous powder of plural-layer structure is 11 to 40 microns, and a mean of the thickness of the thinnest portion of same is 4 microns or more and not exceeding the mean particle size.

6. A nonaqueous electrolyte secondary cell comprising a positive electrode, a negative electrode, and a separator interposed therebetween, said positive electrode having an oxide containing lithium (chemical formula  $\text{Li}_x\text{Mo}_2$ , where M is one or more transition metals selected from Co, Ni, Mn, and Fe, and  $x=0$  or more and 1.2 or less) as an active material, and said negative electrode being made of a negative electrode material that allows lithium ions to repeat intercalation and deintercalation reversibly by charge and discharge, wherein a carbonaceous powder of plural-layer structure with a surface layer of carbonaceous matter being formed therein is used in said negative electrode material, said carbonaceous powder being prepared such that, using a lumpy graphite powder as a nucleus, a surface of this nucleus or the graphite powder is covered with a carbon precursor, which is then fired in an inert gas atmosphere at a temperature within the range of 700 to 2800°C, thereby causing the surface layer of carbonaceous matter to form, wherein said lumpy graphite powder has the following characteristics:

(1) the plane interval (d002) of (002) plane by wide angle X-ray diffraction method is less than 3.37 angstroms, and the size (Lc) of crystallite in a C-axis direction is at least 1000 angstroms or more,

(2) R value, that is the ratio of the peak intensity of 1360 cm<sup>-1</sup> in relation to the peak intensity of 1580 cm<sup>-1</sup> in the argon ion laser Raman spectrum, is 0.3 or less, and the half width of 1580 cm<sup>-1</sup> peak is 24 cm<sup>-1</sup> or less,

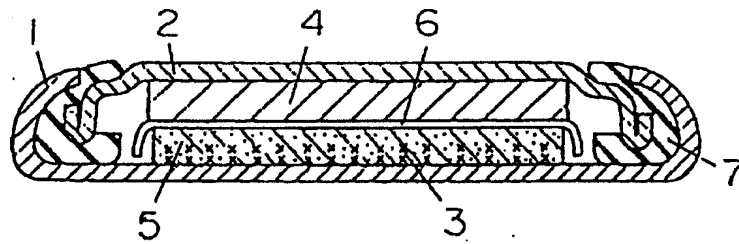
(3) the mean particle size is 10 to 30 microns, and the thickness of the thinnest portion is at least 3 microns or more and not exceeding the mean particle size,

(4) the specific surface area by BET method is 3.5 m<sup>2</sup>/g or more and not exceeding 10.0 m<sup>2</sup>/g,

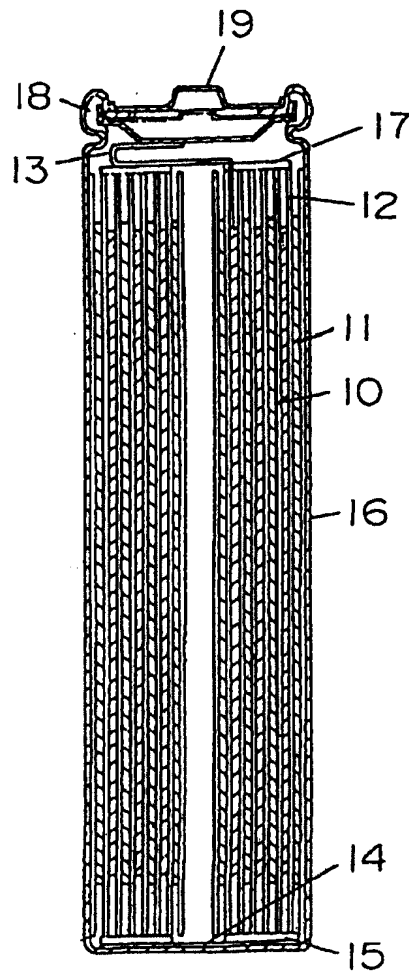
(5) the tapping density is 0.5 g/cc or more and not exceeding 1.0 g/cc, and

(6) the X-ray diffraction peak intensity ratio of (110)/(004) by wide angle X-ray diffraction method is 0.015 or more.

**Fig. 1**



**Fig. 2**





## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/JP98/02400

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>6</sup> H01M10/40, 4/58, 4/02  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>8</sup> H01M10/40, 4/58, 4/02  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 5-74452, A (Asahi Chemical Industry Co., Ltd.), March 26, 1993 (26. 03. 93) (Family: none)	1-6
A	JP, 5-307959, A (Mitsubishi Petrochemical Co., Ltd.), November 19, 1993 (19. 11. 93) (Family: none)	1-6
A	JP, 6-168724, A (Japan Storage Battery Co., Ltd.), June 14, 1994 (14. 06. 94) (Family: none)	1-6
A	JP, 6-295725, A (Sanyo Electric Co., Ltd.), October 21, 1994 (21. 10. 94) (Family: none)	1-6
A	JP, 7-134988, A (Matsushita Electric Industrial Co., Ltd.), May 23, 1995 (23. 05. 95) (Family: none)	1-6
A	JP, 7-335216, A (FDK Corp.), December 22, 1995 (22. 12. 95) (Family: none)	1-6
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search August 6, 1998 (06. 08. 98)		Date of mailing of the international search report August 18, 1998 (18. 08. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02400

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 8-213020, A (The Kansai Coke and Chemicals Co., Ltd.), August 20, 1996 (20. 08. 96) (Family: none)	1-6
P	JP, 9-180720, A (Murata Mfg. Co., Ltd.), July 11, 1997 (11. 07. 97) (Family: none)	1-6
P	JP, 9-199126, A (Matsushita Electric Industrial Co., Ltd.), July 31, 1997 (31. 07. 97) (Family: none)	1-6

Form PCT/ISA/210 (continuation of second sheet) (July 1992)